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One-to-one correspondence between Kekulé and sextet patterns

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The concept of super sextet is clarified and the generalized sextet polynomial in two elements is proposed. Two theorems related to Ohkami-Hosoya conjecture [1] are proved and one novel conjecture is proposed.

Key words: Polycyclic benzenoid hydrocarbon — Kekulé structure — Generalized sextet — Generalized sextet polynomial in two elements — Generalized sextet pattern

1. Introduction

In [2], Ohkami et al. showed the one-to-one correspondence between Kekulé and proper sextet patterns of thin polyhex graphs having at least one Kekulé structure through the "Clar transformation" [3]. But so far, for the general polyhex graphs having at least one Kekulé structure, the one-to-one correspondence problem has not been resolved. In 1983, Ohkami and Hosoya proposed a conjecture [1]: for any polyhex graph having at least one Kekulé structure, there exists one-to-one correspondence between Kekulé and proper sextet patterns. Because they have not given the explicit definition of super sextet, the meaning of the one-to-one correspondence was not sufficiently clarified. In this paper, we give the definitions of generalized sextet and generalized super sextet, propose a generalized sextet polynomial in two elements, and prove two theorems related to Ohkami-Hosoya conjecture. In addition, we propose a new conjecture.

Although we haven't given the final proof of Ohkami-Hosoya conjecture, this paper will make the meaning of the conjecture to be more clarified. In fact, we have proposed a possible way to prove Ohkami-Hosoya conjecture. And we believe that the conjecture will be proved in near future.

2. Some topological properties of polyhex graphs

Like [1], in this paper only the polycyclic benzenoid hydrocarbons are concerned. The carbon atom skeletons of these molecules are expressed by polyhex graphs. Furthermore the discussions are limited to those polyhex graphs having at least one Kekulé structure (or Kekulé pattern). Obviously, the number of vertices of the graphs must be even.

Denote a polyhex graph by $G(V, E)$, where V represents the set of vertices and E the set of edges. $|V|$ and $|E|$ represent the number of vertices and the number of edges in G, respectively. Obviously, all the vertices are of either degree two or degree three. Denote the number of vertices of degree two by g_2, and that of vertices of degree three by g_3. In addition, denote the number of the interior vertices of degree three in G (i.e. the common vertices of three connected hexagons in G) by T_3. The interior of a coronafusene polyhex graph [4] isn't filled by hexagons. Denote the number of the "holes" (not hexagons) in G by k (see Fig. 1).

Some topological properties of polyhex graphs can be easily obtained [5].

$$|V| = g_2 + g_3, \tag{1}$$

$$g_2 = 2n + 4 - T_3 - 4k, \tag{2}$$

and

$$g_3 = 2(n-1) + 2k, \tag{3}$$

where n is the number of hexagons (benzenoid rings) in G. By substituting (2) and (3) into (1), it is easy to obtain

$$|V| = 4n + 2 - T_3 - 2k. \tag{4}$$

Besides,

$$|E| = \tfrac{1}{2}(3g_3 + 2g_2). \tag{5}$$

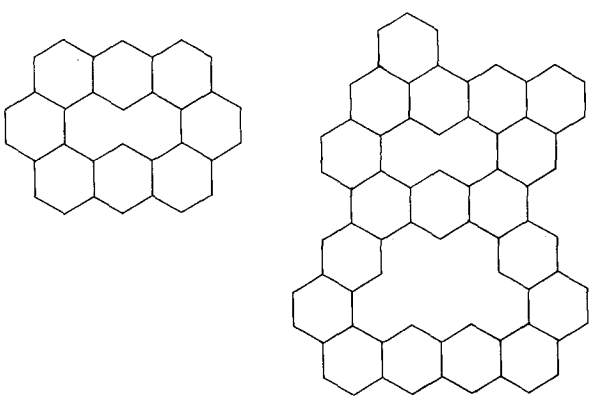

Fig. 1. Holes (not hexagon)

By substituting (2) and (3) into (5),

$$|E| = 5n + 1 - T_3 - k. \tag{6}$$

A Kekulé pattern of a polyhex graph is one, in which all the component points belong to one and only one double bond spanning a pair of adjacent points, or in graph-theoretical terms that such a pattern is a perfect matching (or maximum matching, i.e. a decomposition into 1-factors) of the polyhex graph G [6, 7]. For a perfect matching, the used edge set (double bond) is E_p and the unused edge set (single bond) is E_s. Obviously, [5]

$$E_p \cup E_s = E, \tag{7}$$

$$E_p \cap E_s = \phi \text{ (the vacant set)}, \tag{8}$$

$$|E_p| = \frac{|V|}{2}, \tag{9}$$

and

$$|E_s| = |E| - |E_p|. \tag{10}$$

Substituting (4), (6) and (9) into (10), we have

$$|E_s| = 3n - \frac{T_3}{2}. \tag{11}$$

3. Generalized sextet polynomial in two elements

The necessary definitions are as follows.

Inner polygon in G

It is a polygon in G, and within this polygon there are no more other polygons. Obviously, all the hexagons in G are inner polygons whose vertex number is six. All the interior "holes" (not hexagons) in coronafusene polyhex graphs are also inner polygons whose number in G is k (see Fig. 1). The number of vertices of an inner polygon must be even.

Generalized right sextet and generalized left sextet

Consider an inner polygon P whose vertex number is d. If in a given Kekulé pattern of G, a set of $d/2$ conjugated double bonds are arranged on P, then P is called a generalized sextet in G. And if the vertical edge on the extreme right in P is a double bond, then the generalized sextet is called a generalized right sextet, otherwise a generalized left sextet (Fig. 2). In fact, the definitions of generalized right and generalized left sextet are the extension of the definitions of the proper and improper sextet in [1], respectively.

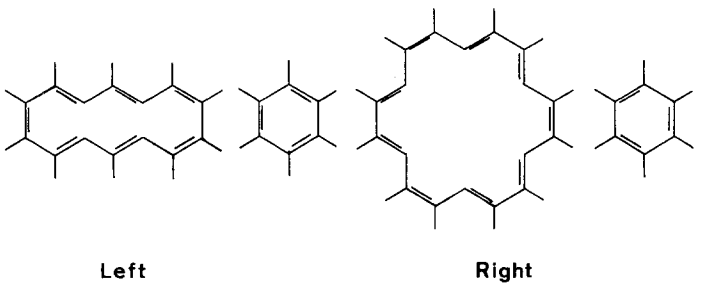

Fig. 2. Generalized right and generalized left sextet

Generalized super sextet

Consider a polygon P' in G. If in P' all generalized sextets (and/or generalized super sextets, as seen later on) and all the fixed bonds [1] connected to them were deleted, the polygon P' could be exposed as a "hole". And if a set of $d'/2$ conjugated double bonds are arranged on the circumference of P' whose vertex number is d', then P' is called a generalized super sextet.

If the vertical edge on the extreme right of a generalized super sextet is a double bond, then the generalized super sextet is called a generalized right super sextet, otherwise a generalized left super sextet. In Fig. 3a there are two generalized right super sextets and in Fig. 3b there is one generalized left super sextet.

If in a Kekulé pattern of a coronafusene polyhex graph G there are some "holes" (not hexgons) to be "generalized sextets," or alternatively, they can be referred to as generalized super sextets.

From now on, the term "generalized sextet" includes "generalized super sextet" unless otherwise stated.

Generalized sextet pattern

A generalized sextet pattern of G is a pattern derived from a Kekulé pattern of G in which all generalized sextets are unchanged, but the remaining double bonds are all transformed into single bonds (Fig. 4).

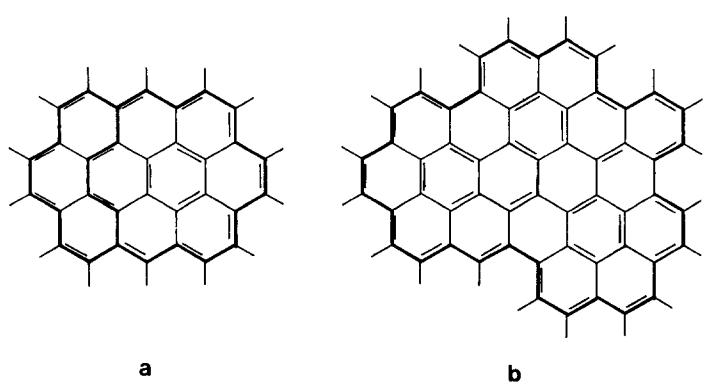

Fig. 3. Generalized super sextet

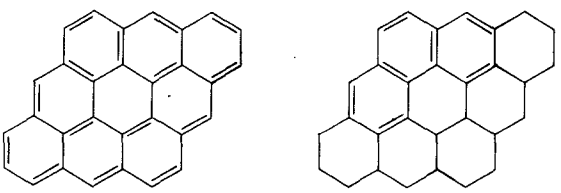

Fig. 4. Kekulé pattern and generalized sextet pattern

Resonant generalized sextet number, $h(G, i, j)$

So called resonant generalized sextet number is the number of ways in which i generalized right sextets and j generalized left sextets can be chosen from G.

Generalized sextet polynomial in two elements

$$H_G(x, y) = \sum_{i=0}^{\max} \sum_{j=0}^{\max} h(G, i, j) x^i y^j, \tag{12}$$

where x and y are simply parameters to hold i and j, respectively. $h(G, i, j)$ can be realized that in all Kekulé patterns of G there are $h(G, i, j)$ and only $h(G, i, j)$ patterns in which there exist i generalized right sextets and j generalized left sextets.

In fact, $H_G(x, 1)$ is equal to the proper sextet polymial $B_G(x)$ in [1], i.e.

$$H_G(x, 1) = B_G(x) = \sum_{k=0}^{\max} r(G, k) x^k, \tag{13}$$

where $r(G, k)$ is the number of ways in which k proper sextets can be chosen from G, and $r(G, 0) = 1$. (See [1]). Besides, define

$$H_\phi(x, y) = 0, \text{ for a vacant graph } \phi. \tag{14}$$

Specifically,

$$H_G(1, 1) = |\det A|^{1/2} = |\det B| = K(G), \tag{15}$$

where A is the symmetrical adjacency matrix of G, but B is the non-symmetrical matrix in the form expressed by Ham [8], having vertices of the starred set as row headings, and vertices of the non-starred set as columns headings; entries in both matrices are 1 for adjacent vertices and O for non-adjacent vertices. Equation (15) means that the counting up of all the generalized sextet patterns of G is equivalent to the enumeration of the number of Kekulé patterns of G. As an example of generalized sextet polynomial $H_G(i, j)$, see Fig. 5.

For the reflection or rotation transformation of G [9], in the generalized sextet polynomial (12) only the interchange of x and y is required. In a similar way to

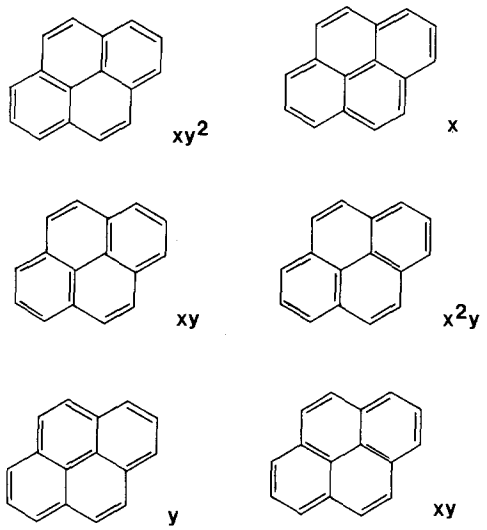

Fig. 5. Terms of a generalized sextet polynomial

that in [1], we can write the recurrence relations of generalized sextet patterns in two elements. For example, for the polyacene series (Fig. 6),

$$H_{G_n}(x, y) = x + y + (n-1)xy. \tag{16}$$

In this paper we will not give the recurrence relations of other specific polyhex series.

4. One-to-one correspondence between Kekulé and generalized sextet patterns

To obtain the one-to-one correspondence between Kekulé and generalized sextet patterns, the key is to prove the following theorem.

Theorem 1. *For any polyhex graph G,* if $G(V, E)$ *has at least one Kekulé pattern, then*

$$h(G, 0, 0) = 0. \tag{17}$$

Proof. Suppose in the case of $i = 0$ and $j = 0$, $h(G, 0, 0) \neq 0$, then there would be at least one perfect matching of G so that in every hexagon of G at most two edges belong to the used edge set E_p (double bond), whereas at least four edges belong to the unused edge set E_s (single bond). Thus

$$|E_s| \geq 4n - |Q|, \tag{18}$$

where n is the number of hexagons in G, and $|Q|$ is the number of common single bond edges of two adjacent hexagons. Obviously, $Q \subseteq E_s$.

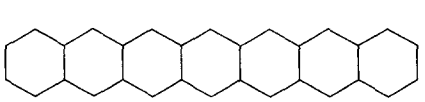

Fig. 6. Polyacene

As stated above, the common vertices of three adjacent hexagons are the interior vertices of degree three, of which the number is denoted by T_3.

Now we call the common vertices of two adjacent hexagons the circumferential vertices (including the circumferential vertices of coronafusene "holes") of degree three. Its number is $g_3 - T_3$.

Because all the vertices in a Kekulé pattern have been saturated by the matching, of three edges terminating on any vertex of degree three two edges belong to E_s and one belongs to E_p. For an interior vertex of degree three, the two single bond edges (belonging to E_s) terminating on it must belong to Q, whereas for a circumferential vertex of degree three at most one single bond edge terminating on it belongs to Q. If in $g_3 - T_3$ circumferential vertices of degree three there are m vertices on which neither of two single bond edges terminating belongs to Q, then we have

$$|Q| = \tfrac{1}{2}(2T_3 + (g_3 - T_3 - m)) = \tfrac{1}{2}(g_3 + T_3 - m). \tag{19}$$

By substituting (19) into (18),

$$|E_s| \geq 4n - \tfrac{1}{2}(g_3 + T_3 - m). \tag{20}$$

By substituting (3) into (20),

$$|E_s| \geq 3n - \frac{T_3}{2} + \left(1 - k + \frac{m}{2}\right). \tag{21}$$

By substituting (11) into (21),

$$1 - k + \frac{m}{2} \leq 0. \tag{22}$$

When $k = 0$ (i.e. in the case of non-coronafusenes) (22) contradicts itself. And so $h(G, 0, 0) = 0$ holds.

When $k = 1$, (22) requires $m = 0$, then the circumferences of coronafusene "hole" forms a generalized sextet. And it is contrary to $i = 0$ and $j = 0$. Hence $h(G, 0, 0) = 0$ still holds.

For a general value of k, from (22)

$$2(k-1) \geq m. \tag{23}$$

As stated above, in the circumferential vertices of degree three there are m vertices connected to their adjacent vertices of degree three by double bond edges.

Let us consider a circumference of a coronafusene "hole". If on it we find a vertex of degree three connected to its adjacent vertex of degree three by double bond edge, on the same circumference of "hole" we can certainly find two or more vertices of degree three connected to their adjacent vertices of degree three by double bond edges.

The reason is very simple. In fact, the number of vertices of the "hole" circumference must be even. If it loses one vertex, it is impossible to do its decomposition

into 1-factors [6, 7]. In this case the circumference of "hole" is not a generalized sextet. Hence as long as a circumference of "hole" is not a generalized sextet, on this circumference there must be at least two vertices of degree three which belong to the m's.

By considering (23), it follows that at most $k-1$ holes (not hexagons) in G are not generalized sextets. In other words, at least one hole (not hexagon) in G is a generalized sextet. It is also contrary to the conditions $i=0$ and $j=0$. Hence $h(G,0,0)=0$ still holds. Q.E.D

Now we can prove the following one-to-one correspondence theorem.

Theorem 2. *For any polyhex G there exists one-to-one correspondence between Kekulé and generalized sextet patterns.*

Proof. According to the definition of generalized sextet patterns, any perfect matching of polyhex graph G (i.e. a Kekulé pattern of G) corresponds to a generalized sextet pattern in which there are i generalized right sextets and j generalized left sextets ($i \geq 0, j \geq 0$ and $i+j \neq 0$).

Inversely, if a generalized sextet pattern with i generalized right sextets and j generalized left sextets is given ($i+j \neq 0$), we can prove that it corresponds to one and only one Kekulé pattern of G.

Let us wipe out all the $i+j$ generalized sextets and the fixed bond edges connected to them. A connected subgraph G_1 of the remainder would be a generalized sextet pattern which should not have any generalized sextet. But according to Theorem 1, $h(G_1,0,0)=0$, in G_1 there would be at least one generalized sextet. The contradition indicates that the remainder does not exist, and Theorem 2 has been proved.

In addition to the above theorems, we propose the following conjecture. Although no rigorous proof can be reached at present time, its validity has been checked by a number of examples.

Conjecture. *For any polyhex graph G,*

$$\sum_{i=1}^{\max} h(G,i,0) = \sum_{j=1}^{\max} h(G,0,j) = 1. \tag{24}$$

If this conjecture can be proved, then the rigorous proof of Ohkami-Hosoya conjecture will be derived easily.

5. Discussion

Unlike [1], in this paper so called generalized sextets include proper and improper sextets. From the graph-theoretical standpoint, the distinction between proper and improper sextet is caused by the orientations of graph. In fact, proper and improper sextet can be mutually transformed by rotation or reflection of the graph [9]. In other words, they have not any material distinction. And their physical and chemical properties should be all the same to each other. And so

it should be more advantageous that many π-electronic properties of isomeric benzenoid hydrocarbons are explained by the generalized sextet polynomial in two elements.

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